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㊹発明の名称　キトサン処理紙

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明　細　書

1 発明の名称

キトサン処理紙

2 特許請求の範囲

1　紙基材にキトサンおよび/またはキトサン塩を処理してなるキトサン処理紙。

2　紙基材が麻パルプを含有したものである特許請求の範囲第1項記載のキトサン処理紙。

3 発明の詳細な説明

【産業上の利用分野】

本発明はキトサン処理紙に関する。さらに詳しくは、本発明はハム、ソーセージなどの食肉製品を充填するファイブラスケーシングに用いられるケーシング用材料として好適に使用しうるキトサン処理紙に関する。

【従来の技術およびその問題点】

従来より、ハム、ソーセージなどの食肉加工品のケーシングには、紙基材に濃度が0.1-2%程度の稀薄なビスコース水溶液を含浸させたのち、凝固液で再生処理し、ついで水洗、乾燥し、さらにビスコース加工を施すことによりえられたケーシング用原反が用いられている。

しかしながら、前記したようにケーシング用原反は複雑な工程を経てえられるものであるから、その製造に要する時間が長く、したがってコスト高となり、さらにビスコース溶液を容易に入手しうる特定の工場でないと該ケーシング用原反を製造することができないという制約がある。また従来より前記ケーシング用材料には大幅な湿潤引張り強度の向上が望まれている。

【発明が解決しようとする問題点】

そこで本発明者らは、前記従来技術の問題点に鑑みて製造上の作業工程が少なく、安価でかつ湿潤引張り強度にすぐれたケーシング用原反をうるべく鋭意研究を重ねた結果、かかる諸条件をすべて具備したケーシング用材料として好適に使用しうるまったく新しいキトサン処理紙

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CHITOSAN-TREATED PAPER

Claims:

1. A chitosan-treated paper comprising a base paper treated with chitosan and/or a chitosan salt.

2. A chitosan-treated paper according to claim 1 werein the base paper contains hemp pulp.

Detailed Description of the Invention:

[Industrial field of utility]

This invention relates to a chitosan-treated paper. More particularly, it concerns a chitosan-treated paper suitable for use as a casing material, specifically for fibrous casings to be filled with processed meat as hams, sausages, or other meat products.

[The prior art and problems]

For the casings of processed meat products such as hams and sausages, casing stocks have been used which are prepared by impregnating base paper with a dilute aqueous solution of viscose at a concentration of only about 0.1-2%, regenerating with a coagulant liquor, water washing, drying, and further viscose-treating the paper.

Since the preparation of casing stocks involve such complex process steps, it takes much time and accordingly the cost is high. Another

limitation is that the casing stocks cannot be made except at particular mills where viscose solutions are easily available. Also, there has been demand for a remarkable increase in the wet tensile strength of casing materials.

[Problems the invention is to solve]

In view of the above, the present inventors have made intensive investigations in search of a casing stock which could be made by fewer process steps, at lower cost, and yet with greater wet tensile strength than heretofore. They have now found, as a result, a novel chitosan-treated paper useful as a casing material which meets all the requirements of the prior art. The present invention is based upon this discovery.

[Means for solving the problems]

Briefly, the invention relates to a chitosan-treated paper comprising a base paper treated with chitosan and/or a chitosan salt.

[Functions and examples]

For the purposes of the invention the term "chitosan-treated paper" is used to mean base paper treated with chitosan and/or a chitosan salt.

The base paper to be used under the invention is any of paper, nonwoven cloth, and the like made, e.g., from wood pulp of wood fiber such as bleached kraft pulp, hemp pulp of hemp fiber, or from their mixture pulp.

The chitosan-treated paper according to the invention is desired to contain hemp pulp which imparts alkali resistance and tensile strength. Because this adds to the cost, it is advisable to adjust the hemp pulp content suitably depending on the weight and wet tensile strength of the

objective chitosan-treated paper. Thus, while the base paper to be used in the present invention may be made solely from wood pulp or hemp pulp, one made from a pulp mixture usually is preferred. The desirable mixing ratio (wood pulp/hemp pulp) by weight normally ranges from 1/99 to 99/1, preferably from 60/40 to 99/1.

The base paper may contain fibers of paper mulberry *Broussonetia kajinoki*, paper birch *Edgeworthia papyrifera* and the like. The presence of these fibers is as beneficial as that of hemp pulp, because they confer increased alkali resistance and tensile strength on the resulting paper.

Base paper is made from wood pulp and/or hemp pulp by a usually used paper-making process, e.g., wet process, though the present invention is not limited thereto. Desirably, the weight of base paper is suitably chosen according to the intended use of the chitosan-treated paper and there is no general rule. A weight range of 10-30 g/m^2 is common, however.

Chitosan as the impregnant for the base paper is a food additive normally obtained by acid or alkali treatment of a composite of chitin, calcium, proteins, etc. contained in the shells of crabs, lobsters, etc., and further treatment of extracted chitin with strong alkali, followed by deacetylation. A chitosan results from dissolution of chitosan in an organic or inorganic acid. The inorganic acid is, e.g., hydrochloric, nitric, sulfuric, phosphoric, or boric acid. Examples of organic acids are formic, acetic, glucosic, oxalic, succinic, adipic, malic, maleic, fumaric, tartaric, phthalic, isophthalic, terephthalic, and lactic acids. Where the chitosan-treated paper is designed for use as a material for fibrous casings to be stuffed with a meat product, a preferred acid among the

organic and inorganic acids is one usually used as a food additive, e.g., acetic, adipic, malic, fumaric, tartaric, or lactic acid.

As compared with chitosan salts which dissolve readily in water, chitosan is scarcely soluble. Where the latter is employed, a desirable practice is to use it with an aqueous solution of such an organic or inorganic acid as mentioned above. In that case, the proportion of the organic or inorganic acid to chitosan is suitably adjusted within the range of 1-10 times the weight of chitosan.

For the ease of treatment the concentration in the aqueous solution of chitosan or chitosan salt should be 20 wt% or below, preferably 10 wt% or below.

Treatment of base paper with chitosan or a chitosan salt is effected in a variety of ways. For example, chitosan or its salt is mixed with pulp before making the base paper; the base paper is dipped in an aqueous solution of chitosan or its salt; or the base paper is coated with an aqueous solution of chitosan or its salt by brushing, knife coating, spray coating, etc. The invention is not limited to such techniques; other methods may be adopted as well.

The chitosan or chitosan salt content in base paper is adjusted usually to a range of 0.01-10 wt%, preferably to 0.5-3.0 wt%. If the content is less than 0.01 wt%, the wet tensile strength of the resulting chitosan-treated paper is not appreciably improved. If it exceeds 10 wt%, the chitosan-treated paper tends to become too hard and too costly.

The base paper thus treated with chitosan and/or a chitosan salt is dried to be the chitosan-treated paper of the invention. The drying method

is not specially limited, but a usual practice is the use of a hot air drier, e.g., at a temperature of 90-150°C.

While the paper chitosan-treated in accordance with the invention may be used as it is, it is possible to subject the paper to usual conversion with viscose before use so as to improve its wet tensile strength.

The chitosan-treated paper of the invention is more fully described in connection with examples and comparative examples below, but it is to be noted that the invention is not in the least limited thereto.

Example 1

Base paper weighing about 23 g/m^2 was made from a dispersion of Manila hemp fiber, while controlling the machine direction/transverse direction strength ratio to be 1/1. Next, 5 parts by weight of chitosan was dissolved in a mixed solution of 5 parts by weight acetic acid and 90 parts by weight water. The solution was applied by spray coating to the base paper until the chitosan deposit was 1.5 wt%. The coated paper was dried to obtain chitosan-treated paper, and its thickness, density, and wet tensile strength as physical properties were measured. Table 1 summarizes the results. Following this, the chitosan-treated paper was impregnated with viscose so that the deposit weighed 700 g/m^2, and the viscose was regenerated by coagulation to give a viscose-converted paper. Its wet tensile strength as a typical physical property was determined. The result is also given in Table 1.

Comparative Example 1

The base paper of Example 1 was impregnated with a 1-1.5% aqueous solution of viscose to make a viscose-treated paper. Its thickness,

density, and wet tensile strength were measured as its physical properties. The results are shown in Table 1. The viscose-treated paper was further impregnated with viscose to attain a deposit of 700 g/m^2, and then regenerated by coagulation to make viscose-converted paper. As its physical properties, the wet tensile strength was determined. The result is given in Table 1.

The wet tensile strength was determined in the following way.

(Wet tensile strength of chitosan-treated or viscose-treated paper)

The wet tensile strength of chitosan- or viscose-treated paper was determined in conformity with JIS P-8135 "Method of testing wet tensile strength of paper and cardboard."

(Wet tensile strength of viscose-converted paper)

The test viscose-converted paper was immersed in hot water at about 80°C for 5 minutes, rinsed, dried, and then its wet tensile strength was determined in conformity with JIS P-8135 "Method of testing wet tensile strength of paper and cardboard."

Table 1 indicates that the chitosan-treated paper of the invention attains a substantial improvement in its wet tensile strength upon viscose conversion over conventional viscose-treated paper upon viscose conversion.

Examples 2-5

The procedure of Example 1 was repeated except that the hemp fiber used in the preceding example was mixed with N paper bleached kraft pulp (NBKP) in making chitosan-treated paper and viscose-converted paper. The thickness, density, and wet tensile strength of the chitosan-treated paper and the wet tensile strength of the viscose-converted paper were determined

as their physical properties. The results are given in Table 2.

Table 1

Ex. No.	Weight of base paper (g/m²)	Physical properties of chitosan- or viscose-treated paper			Physical properties of viscose-converted paper	
		Thickness (mm)	Density (g/cm³)	Wet tens str (kg/cm²)	Wet tens str (kg/cm²)	Qty of viscose deposit (g/m²)
1	23.0	85	0.27	0.475	4.17	708
Comp. 1	23.8	80	0.23	0.396	3.83	708

Table 2

Ex.	Manila hemp/NBKP mixing ratio (wt)	Wt of base paper (g/m²)	Physical properties of chitosan- or viscose-treated paper			Phys. properties of viscose-convted paper	
			Thickness (mm)	Dens (g/cm³)	Wet tens str (kg/cm²)	Wet tens str (kg/cm²)	Qty of viscose deposit (g/m²)
2	100/0	23.2	79	0.25	0.452	3.62	704
3	50/50	26.5	83	0.24	0.427	3.36	706
4	30/70	28.1	85	0.24	0.402	3.31	708
5	10/90	28.7	85	0.24	0.347	3.15	706
Comp 2	100/0	23.8	88	0.23	0.396	3.83	708

It will be understood from Table 2 that the larger the Manila hemp content in the base paper the higher the wet tensile strength values of the chitosan-treated paper and viscose-converted paper.

Examples 6-11

The Manila hemp fiber of Example 1 was used and the weight of the base paper was varied as shown in Table 3, but otherwise in the same manner as described in Example 1, chitosan was impregnated to make chitosan-treated paper samples. Their thickness, density, and wet tensile strength were determined. The samples of chitosan-treated paper were further

impregnated with viscose until the quantity of deposit was 500 g/m^2, and the viscose was regenerated by coagulation to obtain viscose-converted paper. As the physical property of the samples of viscose-converted paper, their wet tensile strength values were measured. The results are shown in Table 3.

Comparative Example 2

With the same Manila hemp fiber used in Example 1, a base paper weighing 17.0 g/m^2 was made. It was impregnated with a 1-1.5% aqueous solution of viscose, and the resulting viscose-treated paper was further impregnated with viscose at the rate of 500 g/m^2 to obtain a viscose-converted paper. The wet tensile strength of the viscose-converted paper was determined as its physical property. Table 3 gives the result.

Table 3

Exp. No.	Weight of base paper (g/m^2)	Physical properties of chitosan- or viscose-treated paper			Phys. properties of viscose-converted paper	
		Thickness (mm)	Density (g/cm^3)	Wet tens str (kg/cm)	Wet tens str (kg/cm)	Qty of viscose deposit (g/m^2)
6	16.8	71	0.23	0.374	3.13	506
7	16.1	71	0.23	0.358	2.61	508
8	15.1	69	0.22	0.331	2.76	506
9	13.8	65	0.21	0.312	2.53	504
10	12.8	62	0.21	0.283	2.42	506
11	11.8	60	0.20	0.259	2.15	508
Comp. 2	17.6	84	0.25	0.347	2.48	508

Table 3 makes it clear that the wet tensile strength values of the chitosan-treated paper and viscose-converted paper improve as the weight of the base paper increases.

Examples 12-16 and Comparative Example 3

An aqueous acetic acid solution containing 5% chitosan was added to

and mixed with the same Manila hemp fiber dispersion used in Example 1 so as to attain the deposition rates shown in Table 4. The dispersions thus prepared were used in making chitosan-containing paper samples weighing about 23 g/m^2 under control such that the machine direction/transverse direction strength ratio of 1/1 was attained.

The thickness, density, and wet tensile strength values of the chitosan-treated paper samples obtained in the same manner as in Example 1 were determined. Also, the wet tensile strength of viscose-converted paper samples obtained by impregnating each chitosan-treated paper sample with viscose at the rate of about 700 g/m^2 and then coagulating and regenerating the viscose was determined. Table 4 summarizes the results.

T a b l e 4

Ex.	Weight of base paper (g/m^2)	Qty of chitosan deposit (%)	Phys. properties of chitosan-or viscose-treated paper			Phys. properties of viscose-convrd paper	
			Thickness (mm)	Density (g/cm^3)	Wet tens strength (kg/cm)	Wet tensile strength (kg/cm)	Qty of viscose deposit (g/m^2)
12	23.0	0.02	16	0.27	0.466	4.10	700
13	23.0	0.5	16	0.27	0.472	4.16	704
14	23.0	1.5	16	0.27	0.475	4.17	709
15	23.0	2.0	16	0.27	0.478	4.18	706
16	23.0	3.5	16	0.27	0.476	4.19	700
Comp. 3	23.0	0	16	0.27	0.458	-*	-

* The paper base could not be viscose-converted because it was not resistant to water and alkalies.

It will be seen from Table 4 that the wet tensile strength values of the chitosan-treated paper and viscose-converted paper increase proportionally to the chitosan deposition rate.

[Advantageous effects of the invention]

The chitosan-treated paper according to the invention is lighter in

weight than ordinary viscose-converted paper and yet possesses wet tensile strength satisfactory for practical purposes. This makes it useful as a casing material for processed meat products. The manufacturing process involved being simpler than heretofore, it reduces the unit price of the resulting chitosan-treated paper to an economic advantage.

第 3 表

Paper ↓

実施例番号	紙基材の坪量 (g/m²)	キトサン処理紙またはビスコース処理紙の物性			ビスコース加工紙の物性	
		厚さ (μm)	密度 (g/cm³)	湿潤引張り強度 ⊗ (kg/cm)	湿潤引張 (kg/cm) ㊀	ビスコースの付着量 (g/m²)
6	16.8	73	0.23	0.374	3.13	500
7	16.1	71	0.23	0.350	2.84	500
8	15.1	69	0.22	0.331	2.78	500
9	13.8	65	0.21	0.313	2.53	500
10	13.0	63	0.21	0.283	2.42	500
11	12.0	60	0.20	0.239	2.25	500
比較例 2	17.0	68	0.25	0.347	2.48	500

⊗ wet tensile strength of paper

㊀ wet tensile strength of viscase coated paper